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Dynamics of the β Process in Poly(vinyl chloride)

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ABSTRACT: The dielectric relaxation data of Ishida in the β-process region of poly(vinyl chloride) is represented in terms of the relaxation function proposed by Havriliak and Negami using the multiresponse techniques developed by Havriliak and Watts to evaluate the parameters and their dependence on temperature. These parameters are compared with those reported by the authors on the viscoelastic β process in poly(vinyl chloride). The three dynamic parameters and their dependence on temperature for the two processes are similar though not all of them are within their 95% confidence limits. The dynamics of the dielectric and viscoelastic β process in poly(vinyl chloride) and polycarbonate are compared. The mechanism for the β process is discussed in terms of the polymer segment orientation model (segment flips) proposed by the authors earlier, with the general model of Mansfield and the ring flip model for polycarbonate by Perchak et al.

Introduction

This paper is another in a series of papers directed at a better understanding of chain dynamics in the glass phase of polymers. Some of these papers reported on the viscoelastic β process in poly(vinyl chloride) (PVC)[1,2] or in polycarbonate (PC).[3] Another[4] reported on the tensile yield properties of PVC as a function of molecular weight, strain rate, and temperature using an approach first proposed by Eyring and co-workers,[5] then extended by Roetling to some polyacrylics[6,7] and to poly(propylene),[8] and also applied to PVC by Bauwens-Crowet et al.[9] In another paper a comparison between the viscoelastic and published dielectric relaxation data of Smith et al.[10] for PC was reported.[11] The approach taken in these papers is based on the following: First the dielectric and viscoelastic β processes are represented in terms of an expression first proposed to represent dielectric α and β relaxation processes. Then tensile yield studies are represented in terms of Roetling's modification of Eyring's model. Finally, the activation energies from the various processes are compared.

There are two important reasons for such an study. First, thermodynamic theories[12] of the glass transition temperature such as those based on the pioneering work of Gibbs et al.[13] seem to suggest that the glass phase is a motionless state, similar to crystals in which polymer chains are "frozen-in place" so that all long-range motions are prohibited. The β process in polymers, usually measured at low strains, ca. 0.1%, and in the glass phase is often considered to be an oscillation about some mean or fixed equilibrium position. This view cannot not represent the mechanism for the large deformations encountered during tensile yielding. This immobilized view of the glass phase is in contradiction to the (limited) correlation observed between the tensile yield studies and viscoelastic as well as dielectric results cited above. Mansfield[14] proposed a jumping model for dielectric α and β dispersions in polymers that is remarkably similar to Eyring's[5] for tensile yielding or Bueche's model[15] for segmental jumping. Such studies may provide a penetrating view of the polymer chain dynamics that occurs in the glass phase.

While the first reason is fundamental to the understanding of the polymeric glass phase, the second reason for such comparative studies is for practical reasons. Many ASTM-type impact tests that characterize the toughness of polymers do not give results that are interpretable to the polymer scientist in terms of polymer structure or chain dynamics. A simple analysis[16,2] of these tests suggest that they essentially measure the energy to break while the specimen is loaded in tension at not only high strain rates but also strain rates that depend on test methods. In addition test specimen preparation, i.e. milling, bottle blowing, is an important aspect of this test. In other words the connection between ASTM impact tests and polymer chain dynamics of the glass phase may be the pioneering work of Eyring and his rate theory that is based on Maxwell–Boltzmann statistics.

The objective of this work is to analyze the dielectric relaxation data for the β process of PVC reported by Ishida[17] and compare them to the viscoelastic results reported by the writers in terms of the concepts mentioned above. In addition the dynamics of the β processes in PVC and PC will be compared.

Estimation of the Parameters

Dielectric Data. A complex plane plot for PVC taken from the work of Ishida[17] covering the temperature range that defines the β process and used in the analysis is given in Figure 1.

Numerical Data. Havriliak and Negami[18] proposed eq 1 to represent the complex dielectric constant, $\epsilon^*(\omega)$, as a function of radian frequency $\omega = 2\pi f$ where f is in hertz, at constant temperature. In this expression, $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ is the complex dielectric constant and $\epsilon'(\omega)$ is the real or storage part of the complex dielectric constant while $\epsilon''(\omega)$ is the imaginary

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \{1 + (i\omega\tau_0)^\alpha\}^{-\beta} \qquad (1)$$

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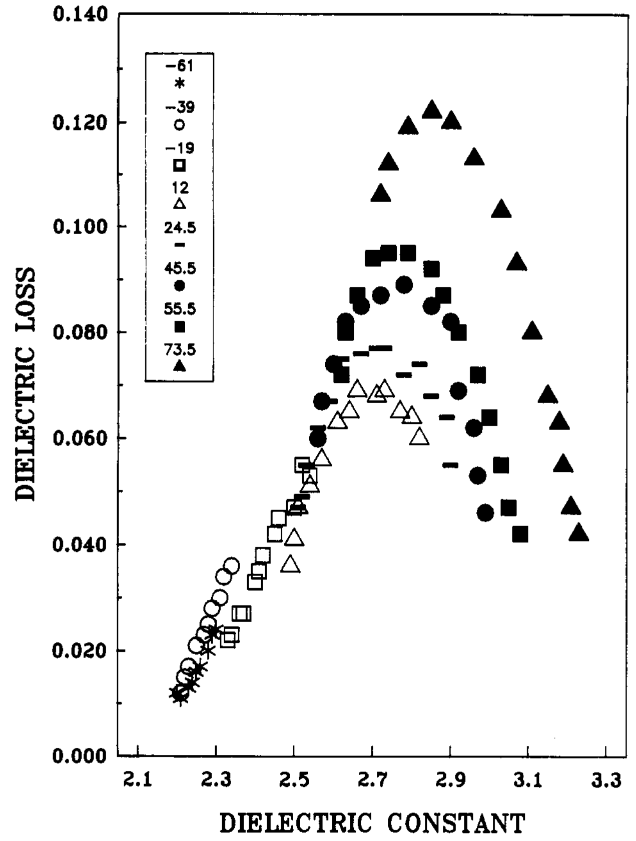

Figure 1. Complex plane plot of poly(vinyl chloride) in the β-process region. The different temperatures are listed in the legend.

or loss part of the complex dielectric constant and $i = (-1)^{1/2}$. The parameters of eq 1 and their dependence on temperature are determined by using methods based on multiresponse techniques.[19,20] In this method the variation of the complex dielectric constant with frequency and temperature is pooled to form a single data set. The complex dielectric constant is assumed to be given by eq 1 while the temperature dependence of the five parameters is assumed to be given by eq 2–6.

$$\epsilon_0 = I_1 + C_1(T - T_0) \quad (2)$$

$$\epsilon_\infty = I_2 + C_2(T - T_0) \quad (3)$$

$$\log(\tau_0) = I_3 + C_3(RK - RK_0) \quad (4)$$

$$\alpha = I_4 + C_4(T - T_0) \quad (5)$$

$$\beta = I_5 + C_5(T - T_0) \quad (6)$$

Both sides of eq 1 are unitless, and the parameters on the RHS will be referred to as the dynamic parameters, while those on the LHS will be referred to as the magnitude parameters. In these expressions T is in °C, T_0 is a reference temperature, chosen to center the experimental data at $T - T_0 = 0$, $RK = 1000/(273 + T)$, $RK_0 = 1000/(273 + T_0)$, and finally $\tau_0 = 1/f_0$, or $\log(\tau_0) = -\log(f_0)$. These equations, except for eq 4, assume a linear dependence of the parameter on temperature, while eq 4 is essentially an Arrhenius plot. In this way it is not necessary to have a complete frequency range to define the parameters.

Results

Attempts to regress the data using a reference temperature of $T_0 = -50$ °C, which is the same reference temperature used in the analysis viscoelastic relaxation data, failed because this temperature was to the extreme side of the experimental dielectric data range. Changing the reference temperature to 12 °C led to immediate convergence. The results of this analysis, assuming neither α or β to be temperature dependent, are given in Table I as case I. The scaled determinant could be reduced by 50% assuming β to be temperature dependent. These results are also given in Table I under the column labeled case II. Attempts to further reduce the scaled determinant by assuming α alone or α and β together to be temperature dependent failed. The best model to represent the dielectric relaxation data of Ishida is case II in Table I. The parameters in case II were converted to a reference temperature of -50 °C, i.e. case III by means of a simple algebraic manipulation. Confidence limits ans other statistical quantities are assumed to be independent of any reparameterization of eq 2–6 and are carried over from case II to case III. A comparison of experimental and calculated results are given in Figure 2 for the real case and Figure 3 for the loss case.

The parameters α and β are formally related to the distribution of relaxation times by means of eq 7.[18] In

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \{1 + (i\omega\tau_0)^\alpha\}^{-\beta} = \int_{-\infty}^{\infty} F(\tau/\tau_0)(1 + i\omega\tau_0)^{-1}\, d\ln(\tau/\tau_0) \quad (7)$$

this expression $F(\tau/\tau_0)\, d\ln(\tau/\tau_0)$ is the distribution of relaxation times function and represents the probability of finding a Debye element in the differential time element represented by the derivative. The Debye element is given by $\{1 + i\omega\tau_0\}^{-1}$. It is also the condition when $\alpha = \beta = 1$ in eq 1. Solution of this integral equation leads to

$$F(y) = (1/\pi)y^{\alpha\beta} \sin(\beta\theta)\{y^{2\alpha} + 2y^\alpha \cos(\pi\alpha) + 1\}^{-\beta/2} \quad (8)$$

where

$$y = \tau/\tau_0 \quad (9)$$

and

$$\theta = \arctan\left\{\frac{\sin \pi\alpha}{y^\alpha + \cos \pi\alpha}\right\} \quad (10)$$

Briefly the parameter α represents the breadth of the distribution of the process while β represents the skewness. The distribution of relaxation times calculated from eq 8 to eq 10 for the values of α and β at the reference temperature estimated from the parameters in Table I are given in Figure 4. The values of α and β are listed in the legend of Figure 4.

Discussion

Five dynamic parameters are required to represent the RHS of eq 1 and their dependence on temperature, i.e. I_3, C_3, I_4, I_5, and C_5. A comparison of these parameters for the dielectric and viscoelastic processes from a statistical point of view is given in Table II. In this table pooled SD (PSD) is defined to be

$$\mathrm{PSD} = \left\{\frac{N_{\mathrm{III}}(\mathrm{SD}_{\mathrm{III}})^2 + N_{\mathrm{IV}}(\mathrm{SD}_{\mathrm{IV}})^2}{N_{\mathrm{III}} + N_{\mathrm{IV}}}\right\}^{0.5} \quad (11)$$

The Roman numeral subscripts refer to the case number in Table I while the values for the parameters are given in the same table. Ratio is defined as the difference divided by PSD. The temperature dependence of the parameter β for the viscoelastic case did not reduce the scaled determinant significantly so that its value in Table I is taken to be zero. A value for the SD was estimated by assuming any curvature to be within the 99% confidence limits of the linear plot. These assumptions

Table I
Relaxation Function Parameters and Their Confidence Limits for Representing the Dielectric Relaxation Behavior of Some Acrylic Polymers

parameter	PVC case I	PVC case II	PVC case III	PVC case IV	PC case V $\epsilon^*(\omega)^{11}$	PC case VI $J^*(\omega)^3$
I_1	2.91	2.94	2.56	0.63	3.062	1.03
SD	0.01	0.01	0.01	0.01	0.004	0.01
C_1	0.0062	0.0061	0.0061	0.0001	0.0004	0.0013
SD	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001
I_2	2.25	2.29	2.17	0.20	2.863	0.57
SD	0.01	0.01	0.01	0.05	0.008	0.01
C_2	0.0008	0.0020	0.0020	-0.0013		...
SD	0.0002	0.0002	0.0002	0.0004		...
I_3	7.0	7.7	-0.63	-2.7	10.2	5.6
SD	0.3	0.4	0.4	1.0	1.5	0.7
C_3	-6.3	-8.5	-8.5	-9.3	-5.4	-7.9
SD	0.2	0.3	0.3	0.7	0.2	0.2
I_4	0.37	0.32	0.32	0.20	0.26	0.21
SD	0.02	0.01	0.01	0.02	0.04	0.01
C_4	...	...	...	...	...	...
SD					...	...
I_5	0.42	0.61	0.37	0.30	0.43	0.51
SD	0.04	0.07	0.07	0.07	0.16	0.07
C_5		0.0038	0.0038	...	...	...
SD		0.0009	0.0009	...	...	...
scal det.[a]	7.7×10^{-7}	4.1×10^{-7}	4.1×10^{-7}	3.5×10^{-7}	9.3×10^{-9}	3.9×10^{-8}
cov[a]						
real[a]	1.0	1.0	1.0	4.5	0.19	0.6
imag[a]	6.1	4.7	4.7	15	34	20
DOF[a]	104	104	104	130	42	193
T_0	12	12	-50	-50	-50	-50

[a] See text for definitions.

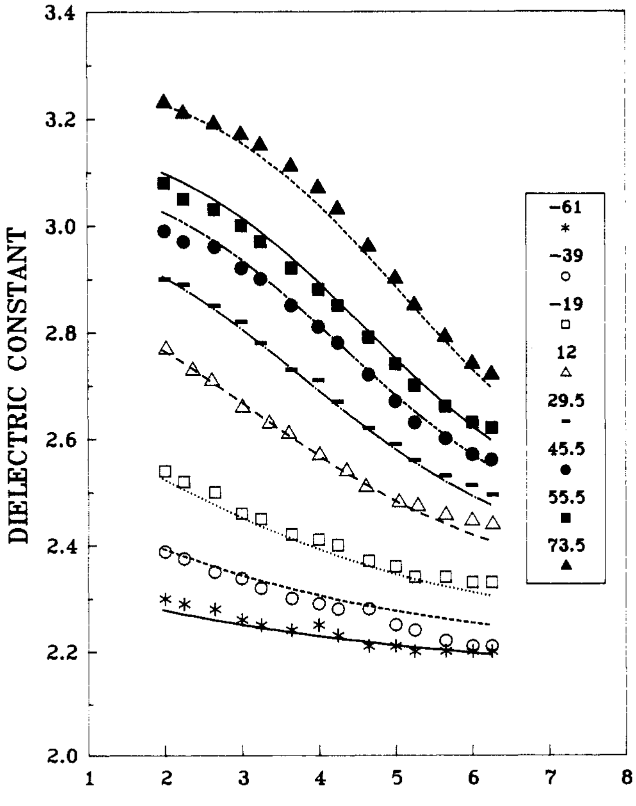

Figure 2. Plot of the experimental (symbols) and calculated (lines) dielectric constants with frequency for the different temperatures indicated in the legend.

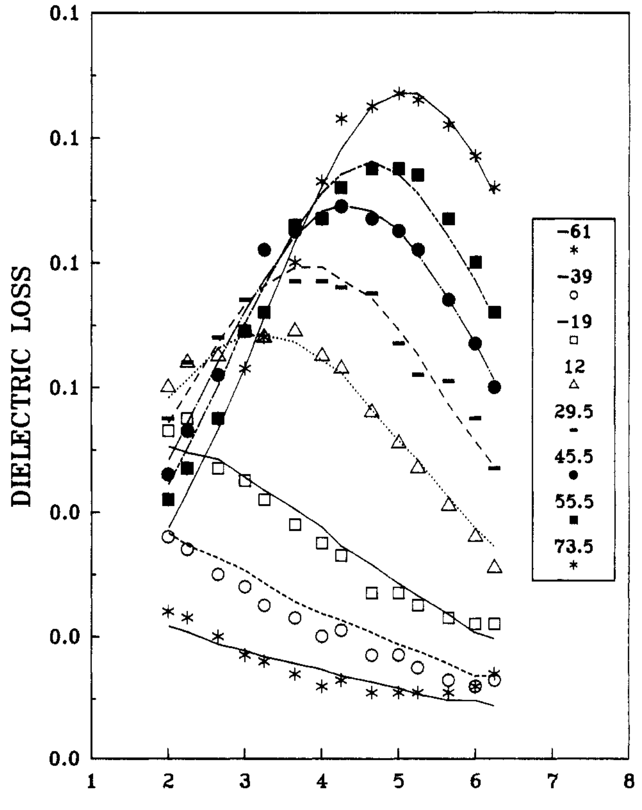

Figure 3. Plot of the experimental (symbols) and calculated (lines) dielectric loss with frequency for the different temperatures indicated in the legend.

were used to estimate the PSD for the temperature dependence of β. Two of the parameters, i.e. C_3 and I_5, are within 1.5 standard parameters estimates and two more, I_3 and C_5, are 2.5 or less while the fifth, i.e. I_4 is outside the 99% confidence limits by a considerable margin. In other words four of the five parameters are within their 99% confidence limits. This agreement suggests strongly that the viscoelastic and dielectric processes are closely

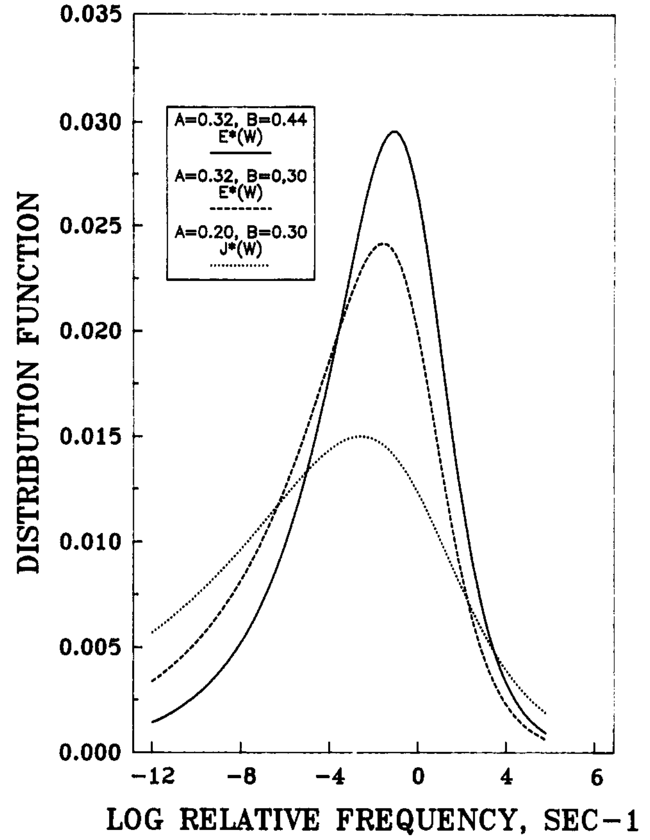

Figure 4. Distribution of relaxation times calculated from eq 7 to eq 10 with the values in the legend.

Table II
Comparison of the Time Parameters and Pooled Confidence Limits of Eq 1 for Cases III and IV in Table I

parameter	PVC case III	PVC case IV	difference III − IV	pooled SD[a]	ratio[a]
I_3	−0.63	−2.7	2.1	0.79	2.5
C_3	−8.5	−9.3	0.8	0.56	1.4
I_4	0.32	0.2	0.12	0.016	7.5
I_5	0.37	0.30	0.07	0.07	1
C_5	0.0038	0	0.0038	0.0016	2.3

[a] See text for definitions.

related, though not necessarily identical. This agreement also suggests that both have a common molecular origin and that the mechanism of the viscoelastic β process is not associated with some macro structure that is independent of the molecular dipole configurations.

One possible cause for the differences noted above is that the test specimens were not prepared in the same way, and it is well-known that the structure of PVC is complicated and sensitive to processing conditions.[21] The dielectric measurements were made on films cast from solution after low molecular weight components were removed by precipitation. The viscoelastic measurements were made on milled compression molded plaques in the presence of processing aids and stabilizers in order to prepare the viscoelastic test specimens. Even so, the parameters are similar, suggesting that the molecular origins or mechanisms are the same for both relaxation processes. In other words the path toward equilibrium after the application of a perturbation stress is probably the same.

The equilibrium, ϵ_0 or J_0, and instantaneous parameters, ϵ_∞ or J_∞, are not expected to be the same since different aspects of the same segment are being measured.

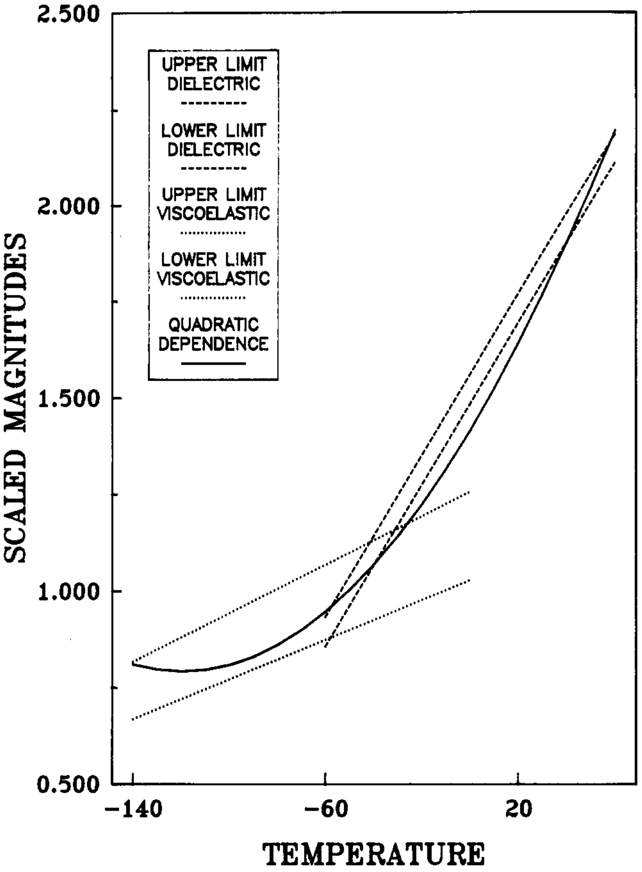

Figure 5. Scaled magnitude of the parameters, defined in the text, for the dielectric and viscoelastic β-process parameters.

However, if these have the same origin, then their temperature dependence may be the same. If we define the incremental value of the dielectric constant associated with the β process to be $\epsilon_0 - \epsilon_\infty$, then a scaled parameter defined

$$\Delta\epsilon_{\beta T} = \frac{(\epsilon_0 - \epsilon_\infty)_T}{(\epsilon_0 - \epsilon_\infty)_{\mathrm{RT}}} \qquad (12)$$

with a similar definition for $\Delta J_{\beta T}$ may be expected to have similar temperature dependences. The subscript RT in eq 12 represents the reference temperature or −50 °C. A plot of $\Delta\epsilon_{\beta T}$ or $\Delta J_{\beta T}$ with temperature is given in Figure 5. The dashed lines represent estimated 95% confidence limits estimated from Table I. The solid line in Figure 5 is the result of representing the variation of the expected value of $\Delta\epsilon_{\beta T}$ and $\Delta J_{\beta T}$ by a quadratic dependence on temperature of the form

$$\Delta\epsilon_{\beta T} = I + C_{\mathrm{a}}(T - T_0) + C_{\mathrm{b}}(T - T_0)^2 \qquad (13)$$

The result of such a curve fitting procedure is represented by the solid line in Figure 5, and it remains almost entirely within the 95% confidence limits of the linear model given in Table I. Attempts to represent the dielectric or viscoelastic data with parameters that depend on a second-order temperature term did not reduce the scaled determinant sufficiently to warrant their inclusion in the model, i.e. eq 2 and 3. In contrast to this individual behavior, it is the extensive frequency range of the combined viscoelastic and dielectric data, about 1×10^{-2} to 3×10^6 Hz, that is required to determine any such temperature dependence.

The authors have proposed[2] a segment flip model to represent the viscoelastic β process in PVC. Havriliak[22] used such a model to represent the dielectric β process

Table III
Dipole Moments for the β Process in Poly(vinyl chloride)

temp, °C	ϵ_0	ϵ_∞	molar vol	Kirkwood's g factor
12	2.94	2.21	48	0.063
−50	2.56	2.16	48	0.032
−150	1.96	1.96	48	0

Table IV
Summary of Activation Energies Determined from Various Measurements

				activatn energy	
polymer	ref	relaxatn process	tensile yield	$J^*(\omega)$	$\epsilon^*(\omega)$
PC	9	α	75.5		117
PC		β	...	20	11
PEMA	7	α	98		(50)
PEMA		β	32		32
PMMA	6	α	81	80	68
PMMA		β	24	22	19
PVC(K55)	4	β	16	13	
PVC(K58)	4	β	15	16	
PVC(K61)	4	β	15	19	
PVC(K69)	4	β	16	19	17

in syndiotactic poly(methyl methacrylate) (s-PMMA). In that work a vector diagram,[23] consistent with infrared evidence was constructed to evaluate Kirkwood's correlation (g) factor. In that study the change in effective dipole moment with temperature was interpreted in terms of a polymer chain segment length that was changing with temperature. The experimental evidence to support that view was that $\Delta\epsilon_\beta$, the relaxation time τ_0 and α varied continuously through the glass transition region. Kirkwood's polar liquid argument, i.e. the so-called reaction field problem, might be applicable to polymers above the glass transition region. In the case of PVC the experimental results are quite different. First, the β-process parameters are known only in the glass phase, and the two parameters α and β are either independent of temperature or nearly so. It is difficult to imagine a change in the effective dipole moment with temperature while its dynamic parameters are independent of temperature. The results of calculating Kirkwood's g factor from the parameters in Table I are given in Table III for a number of temperatures. Temperature dependence of molar volume for PVC was not taken into account. In addition the gaseous dipole moment of methyl chloride was taken to represent the moment of the C–Cl bond with a value of 1.88 Debye units.

Another approach of interpreting the dependence of $\Delta\epsilon_{\beta T}$ on temperature is based on the numerical results of Perchak et al.[24] on the β process (ring flip mechanism) in polycarbonate (PC). In that work he found that the rigidity of the lattice played an important role in permitting or inhibiting the ring flip process to take place. Such a mechanism could be operating in PVC. The dielectric and viscoelastic parameters for the β process for PC are given in Table IV. An inspection of the data in Table I suggests that the dynamic parameters for the β process in both polymers to be similar. First, they both occur in the glass phase, and their 1-s relaxation times are 100 °C or more below the glass temperature. The process in PC is much faster, about 4 decades at the reference temperature. Even so, their shapes in the complex plane, i.e. α and β, are similar. In both cases these parameters are nearly independent of temperature. Finally, in both cases the parameters $\Delta\epsilon_T$ and ΔJ_T decrease with decreasing temperature even though their coefficients may be different. This similarity suggests that as the temperature is lowered, the lattice becomes more rigid, thereby restricting the orientation process.

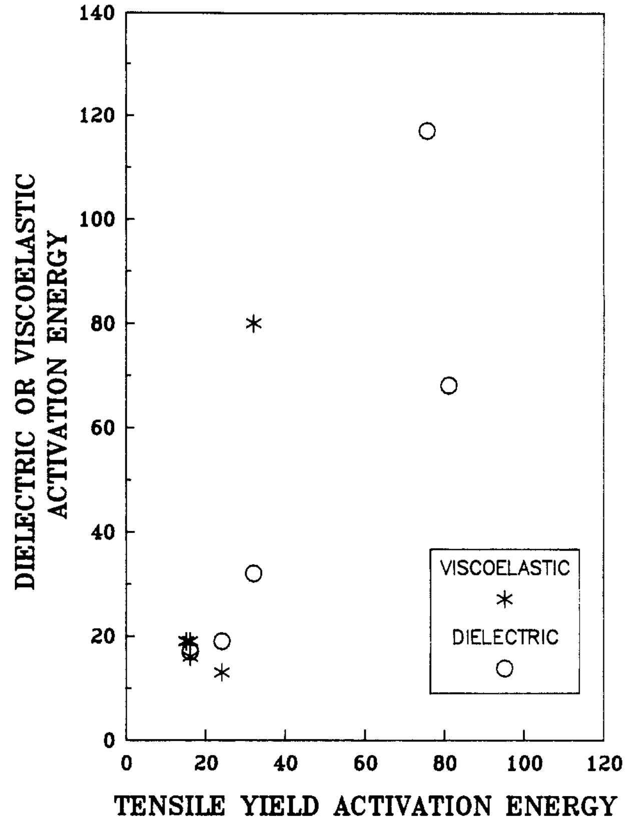

Figure 6. A plot of the activation energy, in kcal mol^{-1}, derived from viscoelastic or dielectric relaxation measurements with those from tensile yield measurements.

Restrictions to the orientation process do not necessarily imply an increase in the correlation parameters for the reasons that follow. The orienting energy O_d or couple between a point dipole moment, $\vec{\mu}$, located on a real polymer segment and the applied electric field $\vec{E}_0$ is generally given by $O_d\ \vec{\mu}_0 \cdot \vec{E}_0$. Placement of that dipole on a real polymer segment in an environment of variable rigidity means that the orientation energy will not entirely be due O_d but will be moderated by a strain energy term, E_s, because a stress field will be set up as the polymer segment rotates to offset the effects of the electric field. For this reason the total orienting energy will be the difference between the two or simply $O_d - E_s$. In other words the total orienting energy, i.e. a reduction of the energy of the system, depends on the magnitudes of the dipole interaction and strain energies of the system. This point of view has been elaborated on in some detail by Havriliak.[25] In such a model the effective moment and its correlation with neighboring dipoles remain the same, but the orientation process is restricted because the ideal or point dipole moment is in fact situated on a real molecule that must distort the environment in order to undergo the usual orientation process, thereby causing an increase in the strain energy.

Mansfield's[14] model is different in detail but similar in kind to Perchak's[23] model because the former analyzes the dynamics of the relaxation process in terms of specific intra- and intermolecular interactions. The loci in the complex plane of Mansfield's model suggests that the intramolecular relaxation times are longer than intermolecular relaxation times in both the PVC and PC cases and for the dielectric as well as the viscoelastic relaxation processes.

A list of activation energies along with the appropriate references determined from tensile yield studies and dielectric and viscoelastic measurements are given in Table IV. The α process for poly(ethyl methacrylate) (PEMA) is in parentheses because Ishida had difficulty in resolving the two processes and its magnitude is in doubt. Brauwens-Crowet et al. did not observe a β process for polycarbonate in their studies. More recently, Havriliak and Pogonowski[3] showed that the β process is too fast under tensile yield experimental conditions to be observed. A plot of the data is given in Figure 6, which shows an overall correlation between the tensile yield activation energy with the dielectric or viscoelastic relaxation.

Conclusions

The results and discussions reported above are based on orientational models for dielectric and viscoelastic relaxation measurements as well as tensile yield measurements. It should also be pointed out that the temperature dependence of the relaxation time as well as its stress dependence is a natural consequence of any jumping process based on Maxwell–Boltzman statistics. This observation is not true for vibration models where the temperature dependence must be obtained by some spurious reasoning process. It should be emphasized that Mansfield's model and Bueche's[15] segmental model are also closely related. Bueche emphasized the temperature dependence of the relaxation time while Mansfield's emphasis is on the time dependence of the segment at constant temperature. Finally both models are consistent with the tensile yield model proposed by Eyring and co-workers and expanded later by Roetling to account for the strain rate and temperature dependence of yield stress, an achievement not to be considered trivial.

Registry No. PVC, 9002-86-2.

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